



NAVAL FACILITIES ENGINEERING SERVICE CENTER  
Port Hueneme, California 93043-4370

# Technical Report TR-2216-ENV

## ESTCP COST AND PERFORMANCE REPORT


### In-Situ Bioremediation of MTBE in Ground Water



January 2003



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# ESTCP Cost and Performance Report

(CU-0013)



## In-Situ Bioremediation of MTBE In Groundwater

September 2003



ENVIRONMENTAL SECURITY  
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14. ABSTRACT This innovative ground water treatment demonstration involved the design, installation, and optimization of a large-scale, bio-barrier for the in situ treatment of ground water impacted by MTBE (methyl-tert-butyl-ether) and other dissolved gasoline components. It was implemented at the Naval Base Ventura County, Port Hueneme, CA to prevent further contamination of ground water by MTBE leaching from gasoline-contaminated soils. The results of this demonstration are of significant benefit to the environmental profession because this project is the first to document a full-scale cost-effective remedy for the in situ treatment of an MTBE-impacted aquifer. Remediation via engineered in situ biodegradation was thought to be an unlikely candidate just a few years ago. This project demonstrates that MTBE-impacted ground water can be remediated in situ via engineered aerobic biodegradation under natural-flow conditions. With respect to economics, the installation and operation costs associated with this innovative bio-barrier system are 66% lower than those of the existing large-scale pump and treat system that was also implemented for containment of the dissolved MTBE plume at Port Hueneme. This project demonstrates that MTBE-impacted ground water can be remediated along with BTEX components via aerobic biodegradation in a mixed MTBE-BTEX dissolved plume. This system has achieved an in situ treatment efficiency of >99.9% for dissolved MTBE and BTEX. Of greater importance is the fact that extensive performance data has been collected and is being used to generate best-practice design guidance and cost information for this technology.					
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## TABLE OF CONTENTS

	Page
1. EXECUTIVE SUMMARY .....	1
1.1 Background .....	2
1.2 Objective of the Demonstration .....	2
1.3 Regulatory Drivers .....	2
1.4 Demonstration Results .....	3
1.5 Stakeholder/End User Issues .....	3
2. TECHNOLOGY DESCRIPTION .....	3
2.1 Technology Development and Application .....	3
2.2 Process Description .....	4
2.3 Previous Testing of the Technology .....	5
2.4 Advantages and Limitations of the Technology .....	6
3. DEMONSTRATION DESIGN .....	7
3.1 Performance Objectives .....	7
3.2 Selection of Test Site .....	7
3.3 Facility History/Characteristics .....	8
3.4 Physical Setup and Operation .....	10
3.5 Sampling/Monitoring Procedure .....	11
3.6 Analytical Procedures .....	12
4. PERFORMANCE ASSESSMENT .....	14
4.1 Performance Data .....	14
4.2 Performance Criteria .....	14
4.3 Data Assessment .....	19
5. COST ASSESSMENT .....	19
5.1 Cost Reporting .....	19
5.1.1 Actual Demonstration Costs at Port Hueneme .....	20
5.2 Cost Analysis .....	21
5.3 Cost Comparison .....	23
6. IMPLEMENTATION ISSUES .....	25
6.1 Cost Observations .....	25
6.2 Performance Observations .....	25
6.3 Scale-up .....	25
6.4 Other Significant Observations .....	25
6.5 Lessons Learned .....	26
6.6 End-User Issues .....	27

## TABLE OF CONTENTS (continued)

	Page
7. REFERENCES .....	27
Appendix A - Sample ESTCP MTBE Biobarrier Demonstration Cost Summary .....	29

## LIST OF FIGURES

	Page
Figure 1. Sample technology implementation at the ASU/Shell pilot-scale test plots, showing major process components .....	6
Figure 2. Site map, showing the extent of the source zone and the MTBE plume .....	9
Figure 3. Monitoring and gas injection wells installed in August 2000 .....	10
Figure 4. Close-up of gas-injection module .....	11
Figure 5. Dissolved oxygen data (in mg-oxygen/L-ground water) .....	15
Figure 6. MTBE concentration data (in mg-MTBE/L-ground water) .....	16
Figure 7. Benzene concentration data (in mg-benzene/L-ground water) .....	17
Figure 8. TBA concentration distribution from March and October 2002 .....	18
Figure 9. Ground water elevation contours .....	18

## LIST OF TABLES

	Page
Table 1. MTBE Loadings for the Different Operating Conditions Along the Biobarrier .....	3
Table 2. MC-100 and SC-100 Technology Development History .....	4
Table 3. Performance Measurements .....	12
Table 4. Analytical Methods .....	13
Table 5. Port Hueneme Biobarrier Installation Costs (500-ft wide system) .....	20
Table 6. Port Hueneme Biobarrier Annual Operation and Maintenance Costs .....	21
Table 7. Future Biobarrier Systems Installation Costs .....	21
Table 8. Variables Impacting Costs Associated with a Biobarrier Installation .....	22
Table 9. Future Biobarrier Systems Annual Operation and Maintenance Costs .....	22
Table 10. Final Remedy Options for the NBVC MTBE Plume .....	24

## ABBREVIATIONS AND ACRONYMS

API	American Petroleum Institute
ARA	Applied Research Associates
ASU	Arizona State University
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
cfm	cubic feet per minute
DO	dissolved oxygen
DoD	Department of Defense
GC	gas chromatograph
IDW	investigation-derived waste
MDL	method detection limit
MTBE	methyl-tert-butyl ether
NBVC	Naval Base Ventura County, Port Hueneme Site
NFESC	Naval Facilities Engineering Service Center
OD	outer diameter
O&M	operation and maintenance
OSHA	Occupational Safety and Health
PELs	permissible exposure levels
QA/QC	quality assurance/quality control
SF <sub>6</sub>	sulfur hexafluoride
SVE	soil vapor extraction
TBA	tert-butyl alcohol
TPH	total petroleum hydrocarbons
VOA	volatile organic analysis
VOC	volatile organic compounds



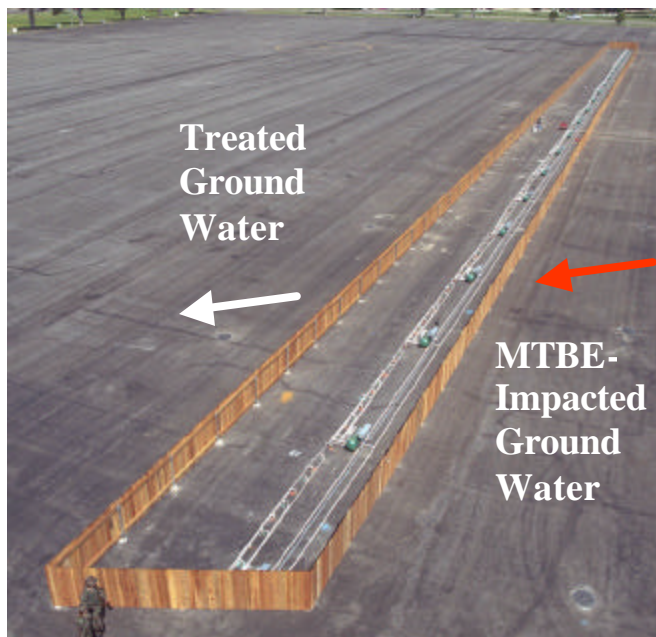
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## 1. EXECUTIVE SUMMARY

### 1.1 Background

This innovative ground water treatment demonstration involved the design, installation, and optimization of a large-scale bio-barrier for the in situ treatment of ground water impacted by MTBE (methyl-tert-butyl-ether) and other dissolved gasoline components. It was implemented at the Naval Base Ventura County, Port Hueneme, CA to prevent further contamination of ground water by MTBE leaching from gasoline-contaminated soils. The Port Hueneme site is well known because the dissolved MTBE plume is already 5000-ft long and 500-ft wide, and because the base has hosted a number of small-scale MTBE treatability studies in recent years.



The results of this demonstration are of significant benefit to the environmental profession because:

- This demonstration project is the first to document a full-scale cost-effective remedy for the in situ treatment of an MTBE-impacted aquifer. Remediation via engineered in situ biodegradation was thought to be an unlikely candidate just a few years ago. This project demonstrates that MTBE-impacted ground water can be remediated in situ via engineered aerobic biodegradation under natural-flow conditions. With respect to economics, the installation and operation costs associated with this innovative bio-barrier system are 66% lower than those of the existing large-scale pump and treat system that was also implemented for containment of the dissolved MTBE plume at Port Hueneme.
- It has been suggested that aerobic MTBE biodegradation will not occur, or not be effective, in mixed MTBE-BTEX (benzene, toluene, ethyl-benzene, and xylenes) dissolved plumes. This project demonstrates that MTBE-impacted ground water can be remediated along with BTEX components via aerobic biodegradation in a mixed MTBE-BTEX dissolved plume.
- This system has achieved an in situ treatment efficiency of >99.9% for dissolved MTBE and BTEX. Samples collected from down-gradient monitoring wells typically now contain <5 ug/L MTBE and non-detectable levels of BTEX components.

Of greater importance is the fact that extensive performance data has been collected and this data is being used to generate best-practice design guidance and cost information for this technology.

## 1.2 Objective of the Demonstration

Specific performance objectives include the following:

Objective	Product
1. Install and operate a full-scale MTBE biobarrier across a mixed BTEX/MTBE dissolved plume, with sections of the biobarrier corresponding to different possible design configurations. At a minimum, design configurations to be tested include a zone seeded with MTBE-degrading organisms and aerated with oxygen gas (bio-augmented), and a zone not seeded with any organisms, but aerated with oxygen gas (biostimulated).	1. A 500-foot long biobarrier was installed at the toe of the immiscible source zone in the mixed MTBE/BTEX dissolved plume at the Naval Base Ventura County, Port Hueneme, CA. The biobarrier was comprised of two different bioaugmented plots (oxygenated and seeded with two MTBE-degrading cultures), and two different types of biostimulated plots (one aerated and one oxygenated). Operation of the aeration/oxygenation system commenced on September 22, 2000, and seeding took place in December 2000.
2. Assess the reductions in MTBE, BTEX, and TPH concentrations achieved by the biobarrier with time.	2. Over 400 wells were installed in August 2000 and approximately 225 of these were used for ground water monitoring. These wells were monitored on a monthly to quarterly basis for dissolved oxygen (DO), MTBE, and BTEX. Periodic quantification of tert-butyl-alcohol (TBA) also occurred. Results are shown in Section 4.1.
3. Assess the effectiveness of oxygen delivery to the target treatment zone.	3. Results from the monthly to quarterly monitoring events are shown in Section 4.1. The oxygen and air delivery created a well-oxygenated treatment zone.
4. Collect economic information. Prepare a technology implementation manual and economic cost model for the technology.	4. The biobarrier technology implementation manual will be completed in December 2002. The economic cost model is presented in Section 5 of this report.

## 1.3 Regulatory Drivers

Regulatory standards for MTBE in ground water have yet to be set on a national level. Most states, however, have established ground water action and cleanup levels for MTBE contamination. In the western states, the level is most often set at 20 ug/L (with the notable exception of California which has established 13 ug/L as its action level and 5 ug/L as a cleanup goal). The eastern states have established action levels ranging from 10 ug/L (VT) to 520 ug/L (LA), with the rest normally falling at 20, 40, or 70 ug/L. Several states have opted to wait for

an EPA MCL to be established (AZ, CO, ND, SD, IA, MS, GA, TN, KY). In order to prevent future contamination, 15 states have laws that will limit or ban the use of MTBE (API 2002).

## **1.4 Demonstration Results**

In this work, the criterion used to determine treatment effectiveness was the comparison of MTBE and BTEX concentrations in ground water up- and down-gradient of the biobarrier treatment zone. Different operational conditions were in effect along the length of the biobarrier (oxygen injection, air injection, oxygen injection + bioaugmentation, etc.), and all of these achieved reductions in influent MTBE (and BTEX, when present) concentrations to less than 5 ug/L. It is important to note that influent concentrations, or relative dissolved hydrocarbon loadings varied along the biobarrier as well. The relative loadings being treated by each of the operating conditions are summarized in Table 1; for reference, the maximum loading was estimated to be approximately 1 g-MTBE/d per ft length of biobarrier, and maximum MTBE concentrations were on the order of 10,000 ug/L.

**Table 1. MTBE Loadings for the Different Operating Conditions  
Along the Biobarrier**

<b>Operating Conditions</b>	<b>Approximate Relative loading</b>
Air-Only (biostimulation)	0.01
Oxygen-Only (biostimulation)	0.05
Oxygen + Microorganisms (bioaugmentation)	1

## **1.5 Stakeholder/ End-User Issues**

There are potential regulatory questions concerning the injection of a microbial culture into an aquifer. Neither of the cultures used in this study, MC-100 and SC-100, were found to be the source of any pathogenic bacteria. The Los Angeles Regional Water Quality Control Board has twice (August 1998 and December 2000) given permission to perform injections of these bacteria into the surficial aquifer at Port Hueneme.

## **2. TECHNOLOGY DESCRIPTION**

### **2.1 Technology Development and Application**

Shell Oil Company (now Shell Global Solutions (US) Inc.) researchers have focused on MTBE biodegradation for over a decade (Table 2). Their work first led to the development of BC-1, an enriched aerobic bacterial culture capable of complete MTBE mineralization (Salanitro, 1994). Using BC-1 in flow through reactors, MTBE was biodegraded from 300 mg/L to <20 ug/l at a hydraulic retention time of 25 hr (Shell Oil Co., 1997b). Laboratory sand columns inoculated with BC-1 achieved similar results with simulated ground water velocities as high as 4 ft/day,

and with solutions containing MTBE and BTEX compounds. Successive generations of the BC-1 culture were named BC-2, BC-3, BC-4, and more recently MC-100. Salanitro isolated a single MTBE-degrading isolate from the MC-100 culture, and this is known as SC-100 or *Rhodococcus aetherovorans*.

**Table 2. MC-100 and SC-100 Technology Development History**

<b>Development Phase</b>	<b>Approximate Time Frame</b>	<b>Sponsors/Participants</b>
Enrichment of mixed culture and lab-scale flow-through reactor tests	1990 - 1993	Shell Oil Company
Development of BC-4 production reactor and large-scale flow-through reactor tests	1993 - 1998	Shell Oil Company
Lab physical model (sand column) studies	1996 - 1998	Shell Oil Company
In situ bioaugmentation pilot-scale demonstration at USN NBVC Port Hueneme, CA facility using the mixed culture MC-100 and oxygen gas injection	1998 – present	Shell Global Solutions /Arizona State University and NFESC
Growth of culture in large-scale reactor (MC-100) and isolation of pure culture (SC-100)	1999 – present	Shell Global Solutions
In situ bioaugmentation pilot-scale demonstration #2 at USN NBVC Port Hueneme, CA facility using mixed culture MC-100 and pure culture SC-100 and oxygenation with air.	2000 – present	Shell Global Solutions /Arizona State University and NFESC

## **2.2 Process Description**

In this technology, a biologically reactive ground water flow-through barrier (the “biobarrier”) is established down-gradient of a gasoline-spill source zone (the “source zone” is delineated by the presence of soils containing free-phase/non-aqueous phase gasoline). Ground water containing dissolved MTBE flows to, and through, the biobarrier. As it passes through the biobarrier, the MTBE is converted by microorganisms to innocuous by-products (carbon dioxide and water). Ground water leaving the down-gradient edge of the treatment zone contains MTBE at concentrations less than or equal to the treatment target levels.

## 2.3 Previous Testing of the Technology

In mid-1998, Arizona State University, in collaboration with Shell Global Solutions and the NFESC installed the first pilot-scale MTBE biobarrier demonstration pilot tests at NBVC. Initially three 20-ft wide demonstration plots were installed; these included: (a) a control plot, (b) an oxygen injection-only plot, and (c) a bioaugmented (MC-100 seeded)/oxygen gas injection plot. All were placed far enough down-gradient of the source zone that ground water contained only MTBE and TBA in the vicinity of the pilot test plots.

Results from those tests were very encouraging. Significant MTBE-concentration decreases were observed in the MC-100 seeded plot within 30 to 60 days. Influent MTBE concentrations ranging from 1,000 – 10,000 ug/L were reduced to non-detect (about 1 ug/L) to about 50 ug/L. The test plots have been operated now for almost 4 years without being re-seeded and without any apparent loss of MTBE-degrading activity. After about 240 days of operation, the oxygen-only plot also showed signs of MTBE-degrading activity. Concentrations in that test plot eventually declined to <100 ug/L levels, suggesting successful biostimulation.

In January 2000 three additional 20-ft wide test plots were installed cross-gradient from the original three test plots. The three additional plots were installed to study the following conditions: (a) MC-100 and oxygenation using air, (b) SC-100 and oxygenation using oxygen gas, and (c) SC-100 and oxygenation using air. Data from this work has yet to be published, but these plots also achieved significant MTBE concentration reductions.

Figure 1 presents a photo of the ASU/Shell Global Solutions/NFESC pilot test plots. It shows the major process components of this technology - gas injection wells, timers, an oxygen generator (or air compressor), gas storage tanks, and ground water monitoring wells.

Details of the first three pilot-scale plots have already been presented by Salanitro et al. (2001). Data from the second three pilot-scale plots using SC-100 will be presented in a manuscript that is currently in preparation.

As the pilot-scale work focused on applications of this technology to an MTBE-only portion of the Port Hueneme plume, this full-scale demonstration focused on application of the technology to a mixed MTBE and BTEX (and other dissolved hydrocarbons) plume.

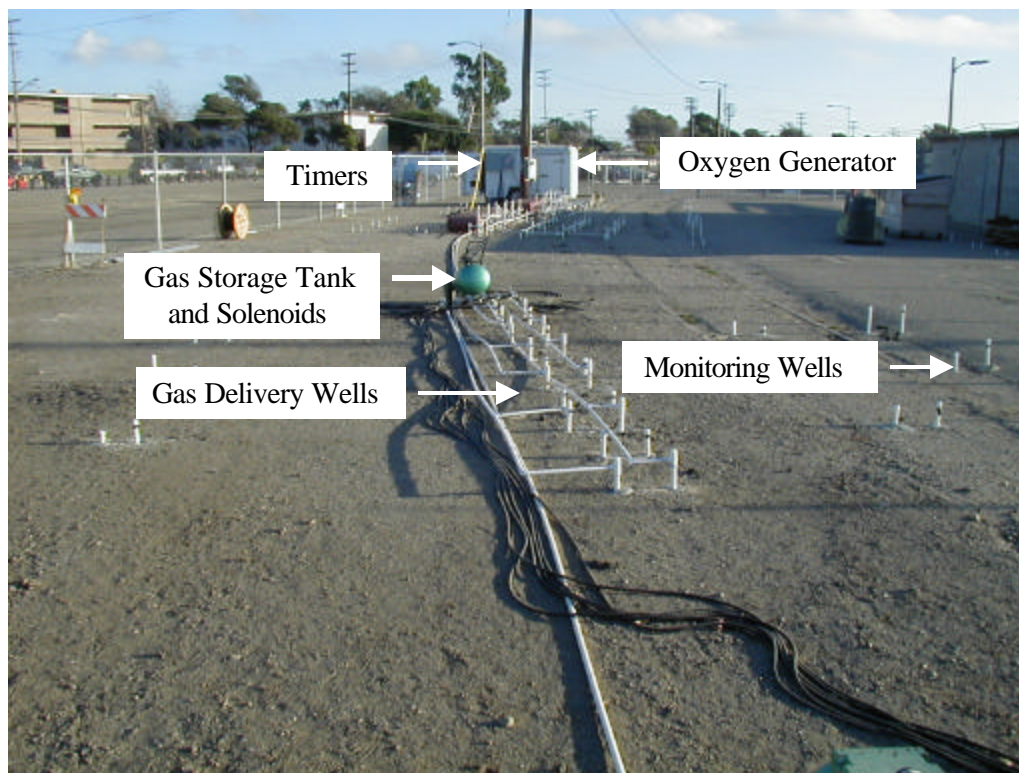


Figure 1. Sample technology implementation at the ASU/Shell pilot-scale test plots, showing major process components.

## 2.4 Advantages and Limitations of the Technology

At this point in time, the profession generally regards pump-and-treat (P&T; ground water extraction followed by above-ground treatment) to be the only proven method for MTBE-impacted aquifer remediation. As conventional above-ground ground water treatment technologies (e.g., carbon adsorption, air stripping, etc.) are much less effective for MTBE than for BTEX compounds, this technology may prove relatively costly and experience suggests that it will have high operation and maintenance requirements.

In comparison, the use of an in situ treatment technology eliminates the need for ground water extraction, above-ground treatment, and discharge. Furthermore, the equipment associated with this bioremediation/bioaugmentation technology includes only those items shown above in Figure 1. In addition, MTBE is mineralized in situ to innocuous products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) by this technology, rather than being transferred to another medium (as is done in most pump and treat and air sparging applications).

The limitation of this technology is that it is applicable only to those settings where: a) the treatment zone can be practicably maintained in a well-oxygenated state, and b) either an MTBE-degrading culture can be delivered, or indigenous MTBE degraders can be stimulated to a level of sufficient activity. Thus, its applicability is limited primarily by the geologic setting (e.g., soil

types, depth to ground water, etc.), in much the same way as many other in situ technologies (e.g., in situ air sparging).

MTBE remediation goals are still being established and revised in many states; drinking water standards range from the low ug/L to 100s of ug/L concentrations. The investigators are not yet aware of any remediation goals established for MTBE biobarrier applications. One possibility is the requirement that ground water leaving the treatment zone meets drinking water standards, while another possibility is that higher concentrations will be acceptable after consideration of dispersion down-gradient of the biobarrier. Pilot tests conducted at Port Hueneme showed that a biobarrier could achieve reduction of concentrations from 1,000 – 10,000 ug/L to <10 ug/L.

The main factor limiting treatment efficiency is expected to be the degree of heterogeneity of the aquifer, the dissolved oxygen distribution, and the MTBE-degrader activity distribution. Thus, different ground water flow paths through a biobarrier could be subjected to different degrees of MTBE treatment. The Port Hueneme site chosen for this demonstration is relatively homogeneous geologically, and the oxygen distribution appears to be relatively homogeneous in the target treatment zone. However, data currently being collected suggests that MTBE degrading activity is heterogeneously distributed throughout the treatment zone.

### **3. DEMONSTRATION DESIGN**

#### **3.1 Performance Objectives**

In this work, the goal is to design and install a system that operates reliably and is capable of consistently reducing MTBE, TBA, and BTEX concentrations to <10 ug/L.

#### **3.2 Selection of the Test Site**

The following general criteria were used for facility selection: (a) willingness of the facility to host the test site and assist with disposal of any waste soils or ground water; (b) ability of the facility to provide personnel to perform weekly checks on the system; (c) easily accessible power and utilities; (d) a good working relationship between the facility and the local environmental regulators; (e) and relatively easy site assess (i.e., no restricted hours for site access or significant foot or vehicle traffic in the area).

The following specific criteria were used for the selection of this demonstration site: (a) a site with sandy soil and a depth to ground water of 10 to 25 ft below ground surface (bgs), (b) a BTEX/MTBE dissolved plume with 100 – 10,000 ug/L concentrations emanating from gasoline-contaminated soils, (c) access to the down-gradient edge of the source zone, and (d) ground water velocities >0.1 ft/d. Condition (a) was necessary so that cost-effective direct-push drilling and well installation techniques could be used and so that ground water sampling could be achieved with peristaltic pumps. Conditions (b) and (c) were necessary as the objective of this demonstration is to demonstrate and assess performance across a mixed MTBE/BTEX dissolved plume. Condition (d) was necessary to ensure that down-gradient water quality changes could be observed within the lifetime of this project.



### 3.3 Facility History/ Characteristics

The USN Naval Base Ventura County NEX service station is at the southeast intersection of 23rd Avenue and Dodson Street (Figure 2). When the NEX service station started operating in 1950, there were two 7,400-gallon underground storage tanks (USTs) with subsequent installations of six additional USTs. All USTs were removed after investigations, starting in December 1984, determined that gasoline was leaking from product delivery lines. Based on inventory records, approximately 4,000 gallons of leaded gasoline and 6,800 gallons of premium-unleaded gasoline were released into the subsurface between September 1984 and March 1985. The gasoline released contained the additive MTBE. The gasoline contaminated the shallow aquifer resulting in a 9-acre gasoline source area plume and a dissolved MTBE plume extending about 5,000 ft. The dissolved plume is, for the most part, under open hardstands (parade ground, parking lots, and storage areas) with a few industrial buildings and one military housing building.

Free-product (mobile) gasoline has not been detected in any of the on-site wells associated with the NEX service station release. Trapped, residual gasoline (as NAPL) is present in the upper three-feet of the aquifer throughout the source zone. Portions of this site have been used for other technology demonstrations, including: ground water pump and treat, ground water recirculation wells, and in situ air sparging/vapor extraction. For the most part these have been conducted several hundred feet up-gradient of the proposed test location and do not affect this demonstration project. To date, no technologies have been applied at the immediate down-gradient edge of the source zone.

Concentrations of MTBE in the vicinity of source zone soils are approximately 10,000 ug/L, decreasing to approximately 1,000 ug/L and lower in moving cross-gradient away from source zone soils. BTEX concentrations are approximately 1,000 ug/L (each component) in the vicinity of source zone soils.

The ground surface at the demonstration site is underlain by approximately 300 feet of unconsolidated clay, silt, sand, and gravel. The geology, within 30 feet of the ground surface, consists of unconsolidated sands, silts, and clays with minor amounts of gravel and fill material. Silty fill material extends from ground surface to about 7 to 9 ft below ground surface (bgs). Below that, medium-grained sands with some gravel are encountered down to 18 to 20 ft bgs, and a clay aquitard is encountered at about 20 ft bgs. The shallow aquifer of interest is unconfined and the depth to ground water is approximately 8 ft bgs, with seasonal variations of about a foot. The gasoline-containing soils are generally found in the sand just below the fill layer from about 9 to 12 ft bgs.

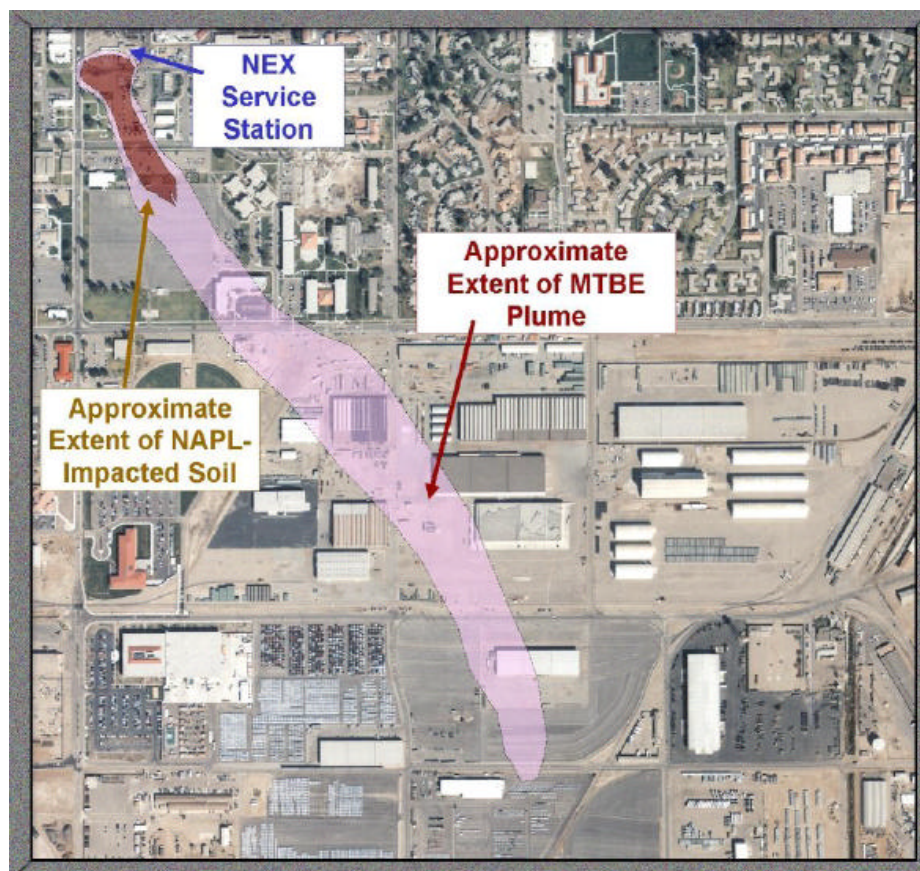


Figure 2. Site map showing the extent of the source zone and the dissolved MTBE plume (north is to the left in this orientation).

In general, ground water in this aquifer flows to the southwest with gradients ranging from approximately 0.001 to 0.003 ft/ft. Transmissivity values ranging from 19,000 to 45,000 gal/day/ft have been reported. Hydraulic conductivity values are estimated to range from 1,300 to 3,000 gal/day/ft. Ground water flow velocity estimates range from 230 to 1,450 ft/year, assuming a porosity of 35 percent. Recent tracer studies conducted by Amerson and Johnson in the vicinity of the proposed site demonstrated ground water velocities ranging from about 280 - 560 ft/year, with velocities increasing with aquifer depth. Based on the observed plume length and time since the gasoline release, a ground water flow velocity estimate of about 300 ft/year can be calculated; however, this value is assumed to be representative of the highest flow velocity for this ground water system. Data from the Equilon-sponsored pilot tests suggest that velocities for some ground water flowpaths could be 1/3 to 1/10 of the values discussed above.

### 3.4 Physical Set-up and Operation

- In May 2000, 19 soil cores and over 50 ground water samples were collected in order to delineate the down-gradient edge of the source zone (i.e. soils containing free-phase/NAPL gasoline), the lateral extent of the dissolved MTBE/BTEX plume, and the longitudinal extent of dissolved BTEX contamination.
- Soil for MTBE degrader activity microcosm studies was collected in June of 2000. These soils were split between ASU and Shell researchers. Initial batch test results indicated that half of the soil cores contained MTBE-degraders, with noticeable vertical heterogeneity in a single core.
- The monitoring wells and gas injection system were installed in August 2000 following the arrangement shown in Figure 3. The aeration/oxygenation system consisted of 21 identical modules; each module consisted of a satellite gas injection tank and 6 solenoid valves. Each solenoid valve was connected to a pair of shallow or deep gas injection wells (screened from either 14-15 ft bgs or 18-20 ft bgs). Figure 4 shows an operating module with all the components labeled. The solenoids are controlled by a series of automatic timers; these allow each satellite tank to fill with gas (either oxygen or air) and then discharge 4 times a day into each well pair (on a 6-h cycle time).

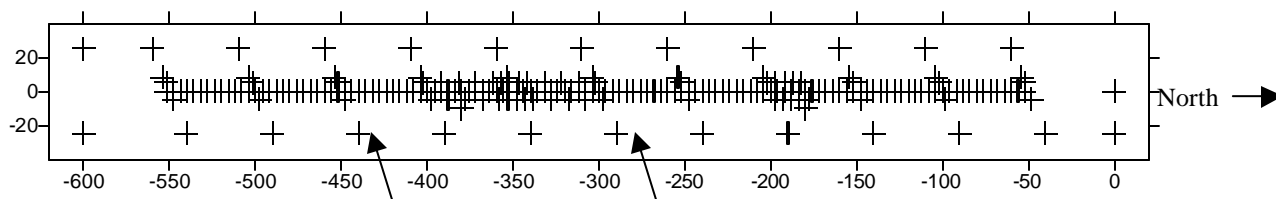


Figure 3. Locations of monitoring and gas injection wells installed in August 2000; each “+” represents paired shallow and deep wells. Ground water flows in the direction of the two arrows below the figure. The lateral dimensions are shown in ft from the northernmost well, and the vertical dimensions are also in ft measured from the gas injection wells row.

- Ground water monitoring began in August 2000 for dissolved oxygen (DO), MTBE, BTEX, and TPH.
- Air/oxygen injection was initiated in September 2000, followed by ground water monitoring for DO, MTBE, BTEX, and TPH.
- Microbial injection of mixed culture, MC-100 along 70 ft of the oxygenated, high dissolved concentration zone occurred in the first week of December 2000. This was followed one week later with the injection of the pure culture SC-100 into another 70 ft of the oxygenated, high dissolved concentration zone.
- From December 2000 to present, the system was operated and monitored as described below.

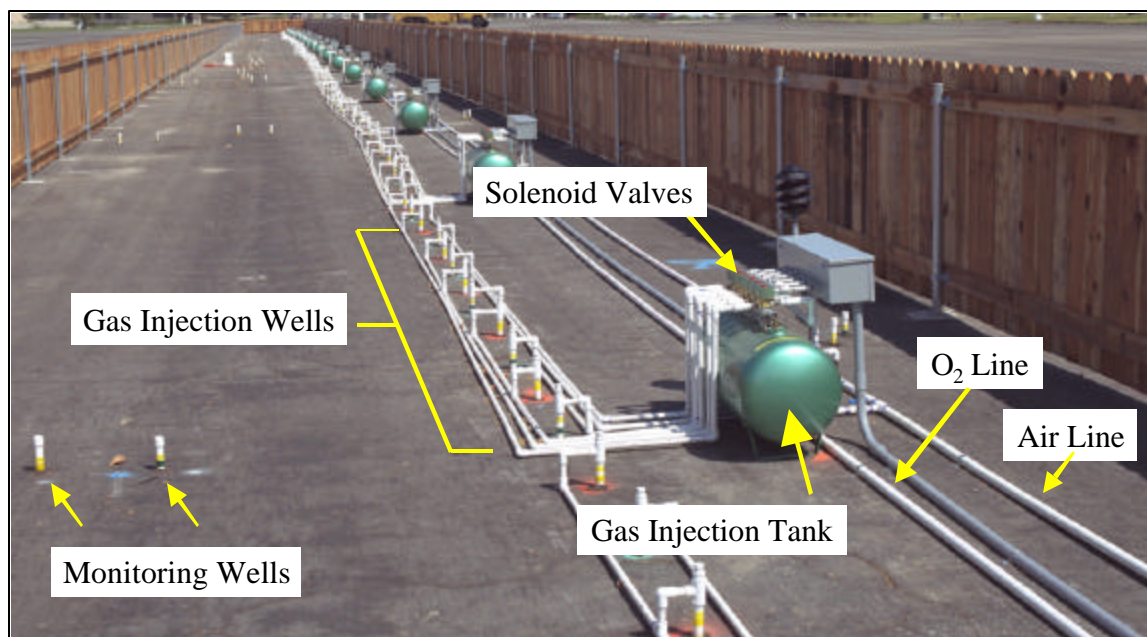


Figure 4. Close-up detail of a gas injection module.

### 3.5 Sampling/Monitoring Procedure

Pre-design site characterization involved the collection of soil and ground water samples in order to confidently delineate the down-gradient edge of the source zone, the lateral extent of the dissolved plume, and the longitudinal extent of dissolved BTEX contamination. Continuous soil cores and ground water samples were initially taken on 50- ft intervals and later on 20-ft spacings, both along and perpendicular to ground water flow. Soil cores were analyzed both visually (for stain) and chemically (using in-the-field methanol extraction followed by GC/FID analysis).

After installation of the monitoring wells (Phase 1 of construction), ground water was sampled and analyzed in August and September 2000. These established baseline/pre-demonstration dissolved oxygen (DO), methyl tert-butyl ether (MTBE), benzene, toluene, ethylbenzene, and xylenes (BTEX) concentrations.

Two months after installation and start-up of the of the oxygen injection system in September 2000, another round of ground water sampling and analysis was conducted prior to inoculation with the MTBE-degrading cultures.

Ground water sampling involved measurement of DO using a flow-through cell and a portable YSI field DO meter. Samples for chemical analysis were collected in zero-headspace VOA vials after DO levels had stabilized and after approximately 1 – 2 well volumes had been pumped from that well. Ground water samples were analyzed for MTBE and BTEX by a GC-FID heated-headspace method. Most analyses were conducted on-site within 48 hours of sample

collection. In a few cases, samples were shipped back to ASU for analysis by purge and trap/GC-MS in order to quantify TBA concentrations.

During the baseline monitoring events, samples were collected from all monitoring wells and from approximately 20% of the gas injection wells. Approximately 10% replicate samples were collected.

Performance monitoring consists of the combination of ground water sampling and system inspection. These are summarized below in Table 3.

**Table 3. Performance Measurements**

<b>Measurement</b>	<b>Purpose</b>	<b>Frequency</b>
Visual inspection	Verification of system operation – track system down-time	Daily
Record of timer sequences and operating pressures	Track operating conditions	Whenever changes are made to the timer sequence or operating pressure
Ground water sampling – dissolved oxygen	Assess performance of the oxygen delivery system	Monthly (initially) - quarterly after three months of operation
Ground water sampling – MTBE, BTEX, TBA*	Assess performance of the biobarrier	Monthly (initially) - quarterly after three months of operation
Ground water elevations	Track changes in ground water levels	Monthly (initially) – quarterly after three months of operation
Tracer Test	Assess ground water flow relative to initial conditions	Once – after three months of system operation

\* measured at 15 and 22 months

### **3.6 Analytical Procedures**

Table 4 lists the analytical methods to be used in this project. These are standard methods already being routinely used for similar projects.

The YSI dissolved oxygen meter was calibrated in air each time it was turned on in the field, per manufacturer's instructions.

GC-FID analyses were conducted on dedicated SRI Instruments Model 8610C gas chromatographs using MxT-1 type capillary columns. The instruments were housed in a dedicated building located approximately 200 ft from the site. The instrument was calibrated each day at least three different concentrations spanning the concentration range of interest (e.g. 100, 1,000, 10,000 mg/kg-soil for methanol-soil analyses and 1 – 10,000 ug/L for dissolved MTBE and BTEX concentrations). In addition, at least one calibration sample was re-analyzed approximately two – to four-times during the day to detect any instrument drift. If area counts

from successive calibration analyses consistently deviated by more than 20% or if retention times varied by more than 0.20 minutes, then the following routine checks are made to the equipment: (a) leaking septum, (b) leaking syringe, and (c) change in gas flows. If those proved not to be the source of error, then a new standard was made and analyzed. If necessary, recalibration over the entire concentration range was repeated. Reporting levels were established based on the calibration results. Based on experience with this instrument, reporting levels of about 100 – 200 mg-TPH/kg-soil are possible for the methanol-soil analysis and reporting levels of 1 – 5 ug/L are possible for the BTEX compounds and MTBE in ground water.

**Table 4. Analytical Methods**

Measurement	Description of Analyses
Dissolved oxygen	Ground water flow-through cell using YSI Model 55 or 95 dissolved oxygen meter
MTBE, BTEX, TBA <sup>*</sup> , TPH in ground water	Heated headspace method: 30 ml sample warmed in 40 ml VOA vial to 50 C followed by 0.5 ml injection of headspace onto a gas chromatograph (GC). Separation by capillary (MxT-1) column and analysis by photo-ionization (PID) and flame-ionization (FID) detectors
TPH in soil (only during source zone delineation)	Methanol extraction of 20-g soil sample in a 40 ml VOA vial followed by direct injection of 2 - 10 uL of extract onto a gas chromatograph (GC). Separation by capillary column and analysis by flame-ionization (FID) detector

\* TBA measured using a GC-Mass Spectrometer at 15 and 22 months

Based on over 4 years of analysis experience at this site, no matrix or environmental interferences were expected during these analyses.

Sample vials were labeled by permanent marker with the well ID and then placed in a cardboard box. The cardboard box was then hand-carried to the field analytical laboratory building, where the vials were placed in a refrigerator until ~1 hour before analysis, when they were placed in a heated water bath to bring them to a consistent temperature (50°C). Samples were analyzed within 48 hours of collection (and typically within 24 hours).

Ground water samples were collected by ASU and NFESC personnel using slow-flow peristaltic Masterflex pumps. Each well had a dedicated polyethylene drop tube and Viton or Norprene tubing was used in the pump heads. The standard procedure was to purge the well until flow-through cell dissolved oxygen measurements stabilized and at least for one well purge-volume (about 1-L for these wells). Zero headspace ground water samples were collected in 40 ml VOA vials having septum caps. This methodology is identical to that used at the Shell/ASU MTBE-biobarrier pilot test sites.

## **4. PERFORMANCE ASSESSMENT**

### **4.1 Performance Data**

Performance data are presented here as a series of snapshots in time (Figures 5, 6, 7, 8, and 9). Each contour plot represents over 225 data points (76 upgradient, 94 downgradient). For each chemical (MTBE, benzene, TPH, and oxygen) the first two contours show the state of the system before the gas injection system was turned on, the third shows the site conditions during the bioaugmentation injection, the last four show concentration distributions at 1, 3, 10, and 15 months after microbial injection.

Overall system performance, as indicated by comparing ground water concentration data to baseline concentration data, showed:

- The aeration/ oxygenation system was sufficient for the demonstration. Site-wide DO concentrations were uniformly below 1 mg-oxygen/L-ground water before the system was turned on. Afterwards, all wells within 5 ft of the gas injection row showed ground water oxygen levels to above 4 mg-oxygen/L-ground water (the level necessary to stimulate and support aerobic degradation). Figure 6 shows the relatively stable dissolved oxygen distribution maintained by the system over a 15 month period.
- Ground water contaminant concentrations leaving the barrier were less than the detection limit after 7 months time.

### **4.2 Performance Criteria**

The performance of this system can be evaluated by answering the following questions:

- Is the zone of aeration/oxygenation stable and does it span the width of the contaminant plume?
- Does influent ground water flow through the biobarrier or around it?
- Are contaminant concentration reduced as ground water flows through the treatment zone?
- Are the contaminant reductions sustainable?

The presence and stability of the zone of aeration/ oxygenation is assessed by inspection of the dissolved oxygen concentration distributions. Ground water oxygen concentrations above 4 mg-oxygen/L-ground water are required for this demonstration.

Contoured water level measurements coupled with contaminant concentrations in ground water at the perimeter wells provide insight as to whether the ground water is going through or around the system.

Concentration distribution plots illustrate the desired level of contaminant degradation achieved and the time sequence provides evidence of treatment stability/consistency.



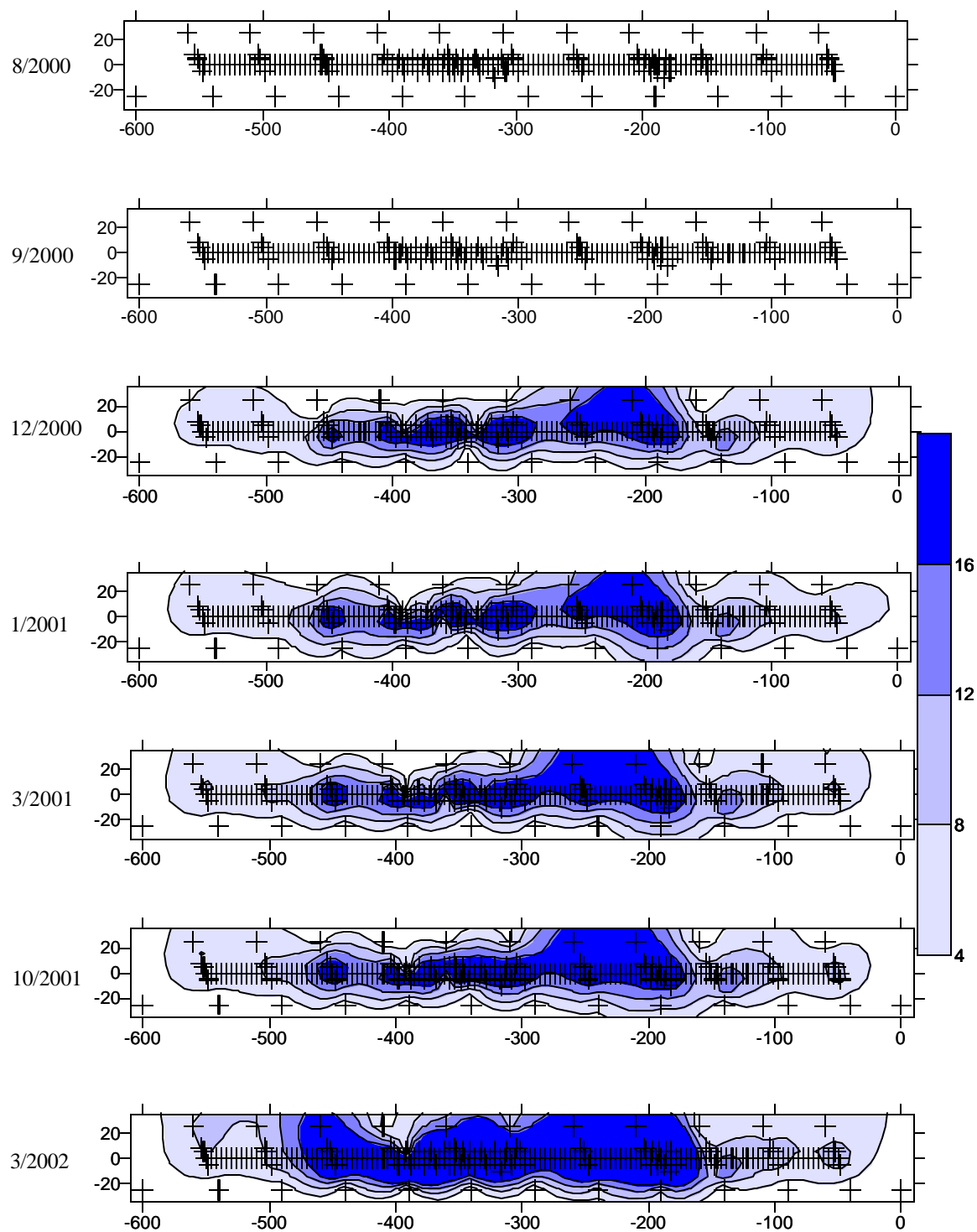


Figure 5. Dissolved oxygen data (in mg-oxygen/L-ground water); each “+” represents paired shallow and deep wells. Ground water flows approximately from the bottom to the top of each figure. Lateral dimensions are shown in feet from the northernmost well, and the vertical dimensions are also in ft measured relative to the position of the row of gas injection wells.



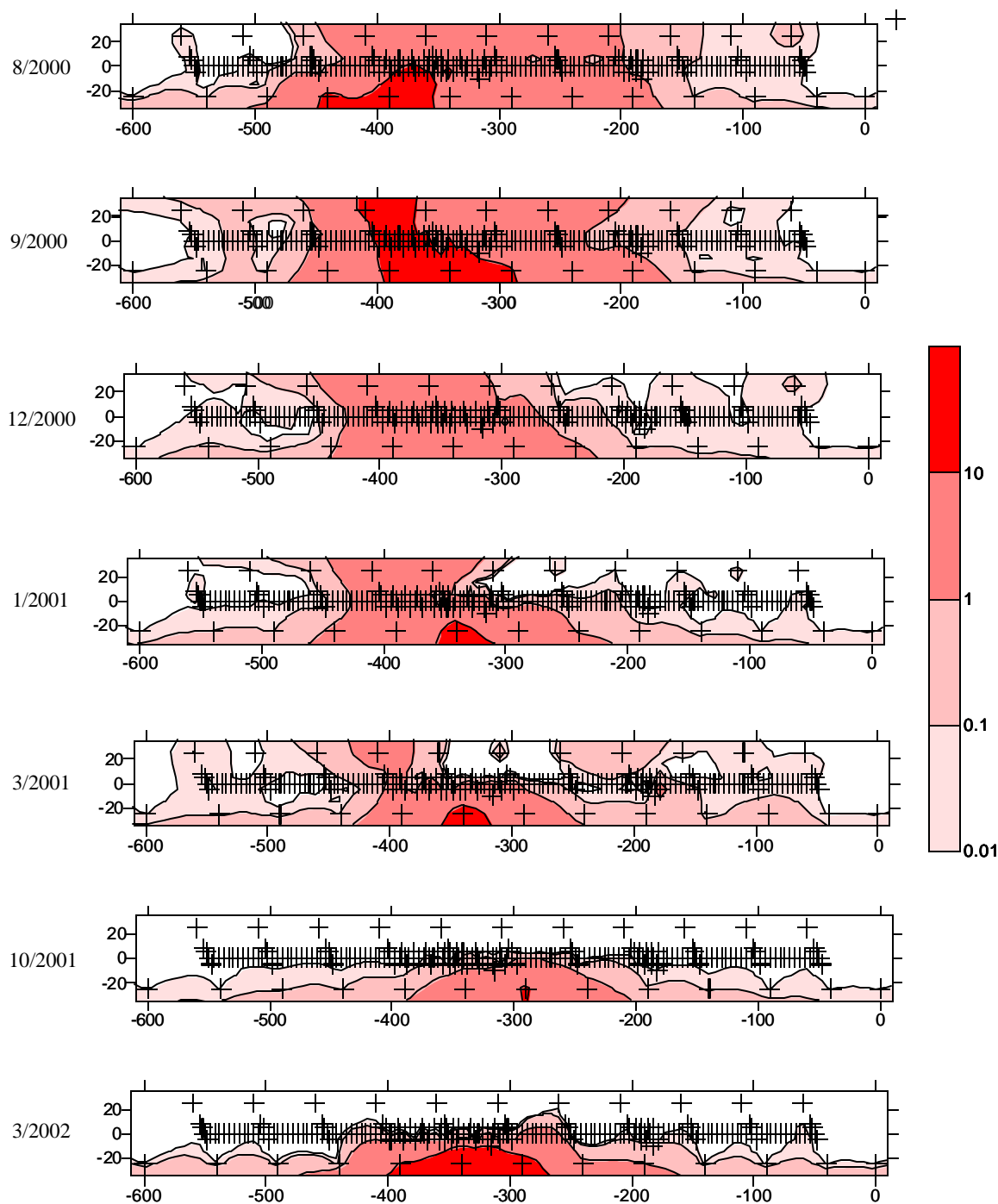


Figure 6. MTBE concentration data (in mg-MTBE/L-ground water); each “+” represents paired shallow and deep wells. Ground water flows approximately from the bottom to the top of each figure. Lateral dimensions are shown in feet from the northernmost well, and the vertical dimensions are also in ft measured relative to the position of the row of gas injection wells.

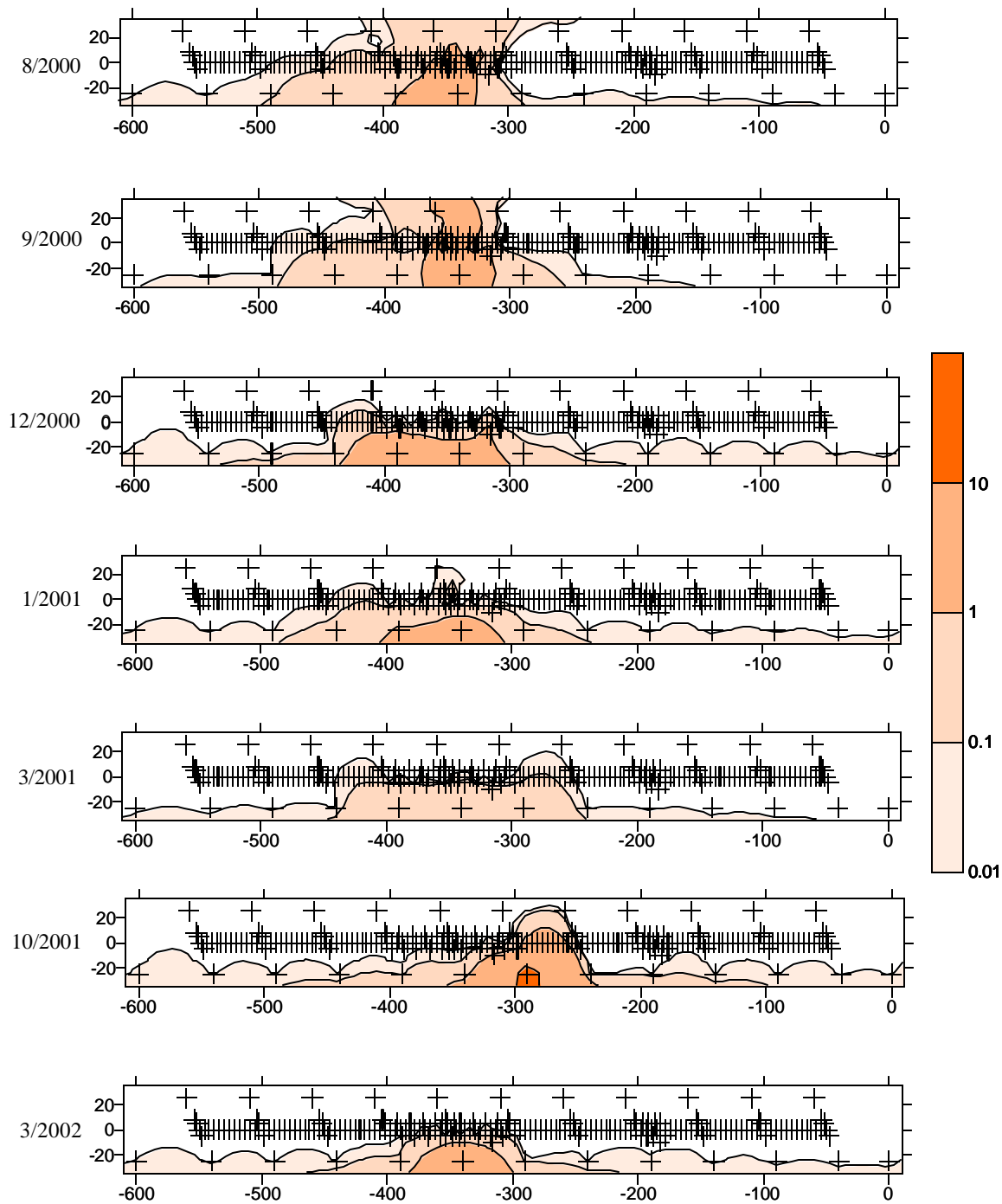


Figure 7. Benzene concentration data (in mg-benzene/L-ground water); each “+” represents paired shallow and deep wells. Ground water flows approximately from the bottom to the top of each figure. Lateral dimensions are shown in feet from the northernmost well, and the vertical dimensions are also in ft measured relative to the position of the row of gas injection wells.

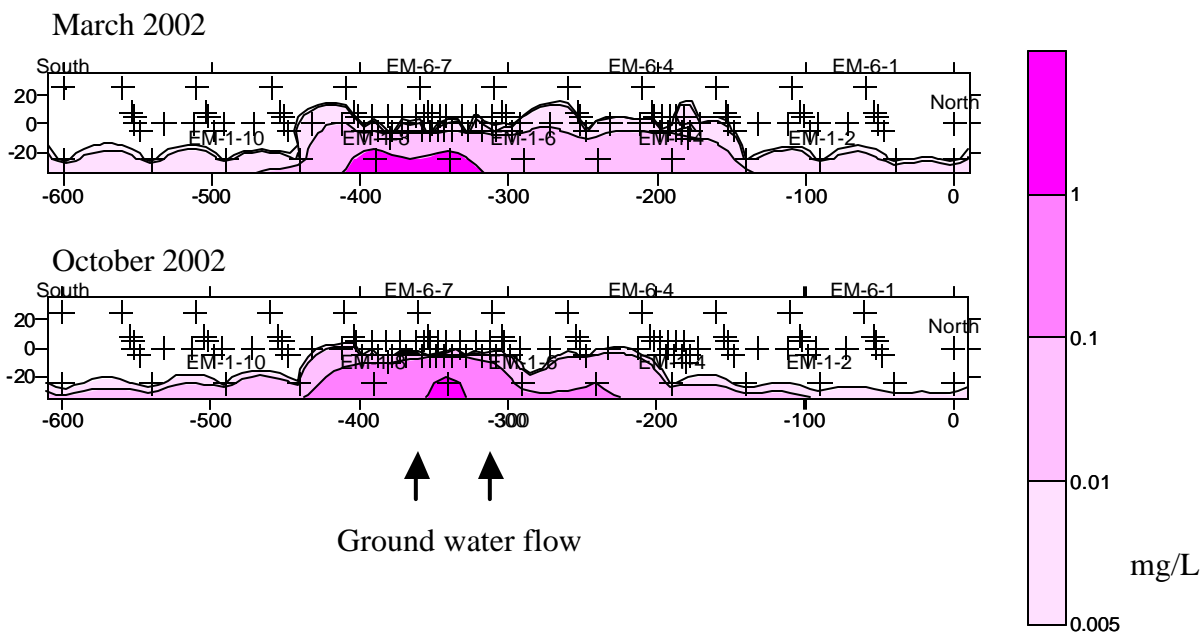


Figure 8. TBA concentration distribution from March and October 2002; each “+” represents paired shallow and deep wells. Ground water flows approximately from the bottom to the top of each figure. Lateral dimensions are shown in feet from the northernmost well, and the vertical dimensions are also in ft measured relative to the position of the row of gas injection wells.

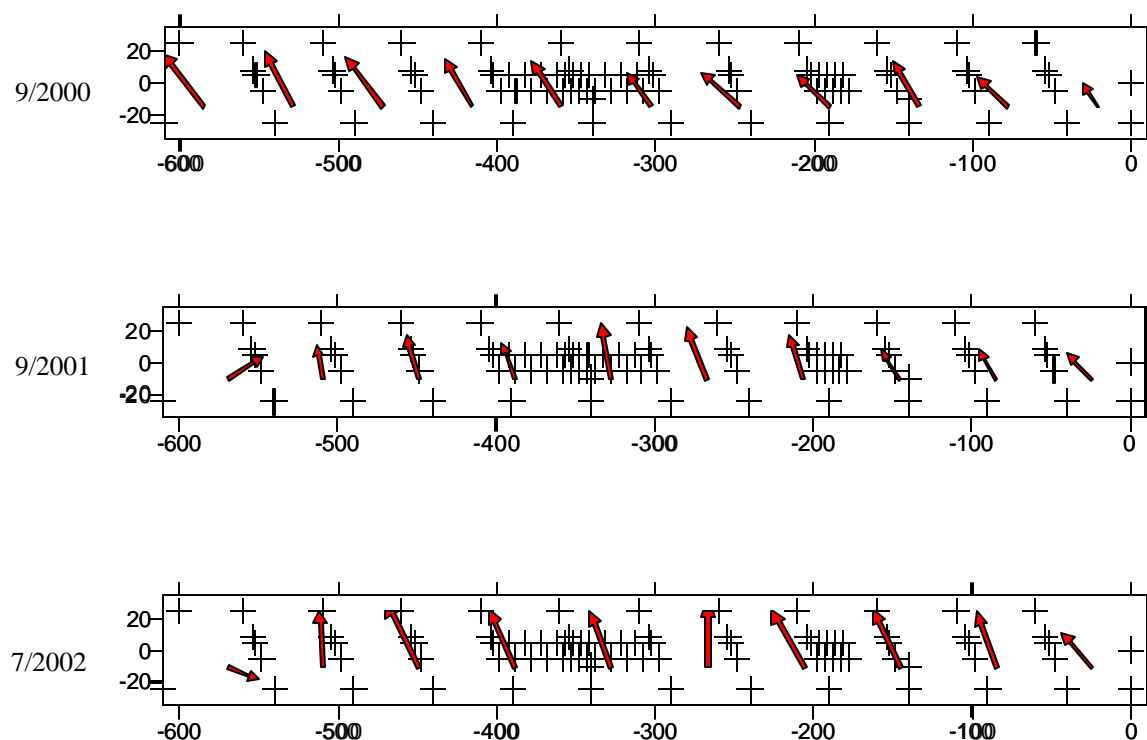


Figure 9. Ground water flow (a) before gas injection, (b) after 1 year of operation, and (c) after 1 year, 10 months of operation. Water levels in the left-hand portion of the barrier often showed the effect of irrigation on the grassy area to the south of the biobarrier.

### **4.3 Data Assessment**

Aeration/ oxygenation was initiated on 22 September 2000. Measured DO data (Figure 6) showed the gas-injection system to be robust and capable of elevating the DO above 4 mg-oxygen/L- ground water, (the target level for aerobic biodegradation ). Levels above 12 mg/L were achieved by the oxygen gas injection, and levels ranging from about 4 to 8 mg/L were achieved by air injection sections of the system.

Measured down-gradient MTBE concentrations declined 1 to 3 months after bioaugmentation (and 4 to 6 months after gas injection started). MTBE concentrations in ground water exiting the treatment system were below detection limits within 7 months (Figure 7).

The dissolved benzene concentration distributions (Figure 8) show a faster response than the MTBE concentrations. Down-gradient benzene concentrations show noticeable decreases within 3 months of the initiation of the air injection system. Since December 2000 effluent benzene concentrations were below detection limits.

TBA concentrations measured in March 2002 show a similar degree of treatment as MTBE and BTEX.

The combination of hydraulic data (Figure 9) and the contaminant concentration distributions demonstrates that no significant bypassing of contaminants occurred during this test.

A full data set from this project is included with the Final Report.

## **5. COST ASSESSMENT**

This section discusses the cost considerations involved in the application of the biobarrier technology to an MTBE plume. Cost reporting for the full-scale biobarrier demonstration, a cost analysis and a cost comparison are discussed in the following sections. A detailed cost projection tool is contained in the Final Report

### **5.1 Cost Reporting**

The site at Port Hueneme is a gasoline-contaminated site located at the edge of the source zone. Ground water is located at a depth of approximately 7 to 9 ft bgs, with the contaminated portion of the aquifer located from the ground water table down to approximately 20 ft bgs. The biobarrier demonstration spans the full width of the Port Hueneme dissolved MTBE plume. At 500 ft wide, this demonstration is several times larger than a typical MTBE plume.

### 5.1.1 Actual Demonstration Costs at Port Hueneme

With the exception of the well installation and electrical installation, ASU and NFESC personnel installed the biobarrier at Port Hueneme over a 5-week period. Table 5 lists the actual installation costs. The biobarrier installation costs were \$307K, at a cost of \$614/linear foot.

**Table 5. Port Hueneme Biobarrier Installation Costs (500-ft wide system)**

<b>Task Description</b>	<b>Materials</b>	<b>Labor</b>	<b>Total</b>
<b>1.0 Biobarrier Installation</b>	<b>\$163,914</b>	<b>\$143,286</b>	<b>\$307,200</b>
1.1 Air & O <sub>2</sub> Delivery System	\$96,917	\$89,603	\$186,519
1.2 Field Laboratory	\$18,239	\$11,477	\$29,716
1.3 Culture Injection	\$48,758	\$42,206	\$90,964

A detailed cost breakdown of the installation costs is contained in Appendix A. The main components of the biobarrier system are the injection/monitoring wells, the injection of the culture and the air and O<sub>2</sub> delivery system.

- Vironex, a drilling company utilizing direct push Geoprobe technology, installed the 426 wells in one week. Working 10-hour days, and sometimes with two rigs and two crews, the crews averaged 47 well installations each day.
- During the culture injection phase, Vironex was able to inject culture across 24 linear feet in a day. Injections were spaced 1-ft horizontally and vertically.
- The oxygen generator cost \$48K with the total costs of the air and oxygen delivery system being \$187K. In order to save project funds, the oxygen delivery system at Port Hueneme was installed mostly above ground (main header lines between the biobarrier and oxygen generator were installed in a trench). Depending on site requirements, an oxygen delivery system could be installed almost completely below ground. At Port Hueneme, it was estimated that it would cost an additional \$170/ft to install the oxygen delivery system underground.
- A small field laboratory was installed at Port Hueneme to conduct the on-site analysis at a cost of \$30K.

During the 2-year demonstration, NFESC and ASU personnel operated and maintained the biobarrier. The annual O&M costs for the biobarrier averaged \$77K a year as shown in Table 6. The oxygen generator compressor failed after 18 months of operation because it was a 220V compressor and the power on the base was 208V. Since 208V power is common on military bases, this has been noted in the lessons learned section of the final report.

**Table 6. Port Hueneme Biobarrier Annual Operation and Maintenance Costs  
(500 ft wide system)**

<b>Task Description</b>	<b>Materials</b>	<b>Labor</b>	<b>Total</b>
<b>2.0 Biobarrier Annual O&amp;M</b>	<b>\$5,460</b>	<b>\$72,383</b>	<b>\$77,843</b>
2.1 Oxygen Generator O&M	\$5,460	\$13,540	\$19,000
2.2 Sampling and Analysis	\$0	\$44,400	\$44,400
2.3 Utilities	\$0	\$14,443	\$14,443

## 5.2 Cost Analysis

Based on the full-scale demonstration costs at Port Hueneme and input from Shell Global Solutions (US) Inc., the projected costs to install a biobarrier at a site range from \$800/linear foot to \$1050/linear foot for aquifers less than 30 feet bgs as shown in Table 7. The costs for a biobarrier are estimated in dollars per linear foot because the purpose of a biobarrier is to cut off a plume so a biobarrier is typically installed across the width of a plume or across the leading edge of a plume. The well installation costs will increase for aquifers greater than 30 feet bgs because the efficiency of direct push technology is reduced, and at some depths conventional drilling and installation techniques would be required. Using the detailed cost projection tool shown in the Excel spreadsheet displayed in Appendix A (and included with the Final Report), the projected future length of the biobarrier system can be adjusted to provide cost estimates for different plume widths. Additional variables that will affect the costs associated with the implementation of a biobarrier are discussed in Table 8.

**Table 7. Future Biobarrier Systems Installation Costs  
(500 ft wide system)**

<b>Task Description</b>	<b>Materials</b>	<b>Labor</b>	<b>Total</b>
<b>1.0 Biobarrier Installation</b>	<b>\$397,810</b>	<b>\$155,286</b>	<b>\$553,096</b>
1.1 Air & O <sub>2</sub> Delivery System	\$90,160	\$79,182	\$169,342
1.2 Field Laboratory	N/A	N/A	N/A
1.3 Culture Injection	\$307,650	\$76,103	\$383,753

**Table 8. Variables Impacting Costs Associated with a Biobarrier Installation**

<b>Cost Variable</b>	<b>Impact</b>
1. Soil Characteristics	1. The installation costs increase for finer-grained soil because the air injection wells have to be spaced closer together.
2. Need for Bioaugmentation or Sufficiency of Biostimulation	2. Based on the results at Port Hueneme, it appears that biostimulation (aeration only) is a viable option. However it can take 6 to 12 months longer for the natural degraders to become well established. A \$5K microcosm test can be conducted before system installation to determine if natural degraders are present at the site. If the site has immediate treatment time constraints imposed on it by a regulator, bioaugmentation may be the only option.
3. Depth to Ground water	3. The direct push technology can be used for aquifers less than 30 bgs. Conventional well installation will increase costs.
4. Width of the Plume	4. Installation costs increase as the treatment width increases. This can be estimated using the cost projection tool found in the final report.
5. Type of Installation Required at the Site (i.e. aboveground or underground)	5. Installing the system underground in a trench will increase installation costs by \$100 - \$150 per linear foot.

Because of the full scale size of the NBVC biobarrier demonstration, the operation and maintenance costs for a future biobarrier system will be very similar to the requirements of the NBVC biobarrier as shown in Table 9. The oxygen generator should be checked 2-3 times a week. The compressor typically runs 8 to 10 hours a day. The utility cost used in these calculations was \$0.14/kWh.

**Table 9. Future Biobarrier Systems Operation and Maintenance Costs (500 ft wide system)**

<b>Task Description</b>	<b>Materials</b>	<b>Labor</b>	<b>Total</b>
<b>2.0 Biobarrier Annual O&amp;M</b>	<b>\$4,460</b>	<b>\$71,063</b>	<b>\$75,523</b>
2.1 Oxygen Generator O&M	\$4,460	\$12,980	\$17,440
2.2 Sampling and Analysis	\$0	\$44,000	\$44,000
2.3 Utilities	\$14,083	\$0	\$14,083

### 5.3 Cost Comparison

In comparison with conventional pump and treat systems, the biobarrier technology is both less expensive to install and has significantly lower long-term operation and maintenance costs. At Port Hueneme, an interim full-scale pump and treat system was installed and operated at the down-gradient edge of the dissolved MTBE plume. The FY02 O&M costs for maintaining the Port Hueneme P&T system are \$250K/year compared to the biobarrier O&M costs of \$75K/year. For the Port Hueneme site, several different treatment options, shown in Table 10, were evaluated for the final remedy of the MTBE plume.

The Navy conducted a Pump and Treat evaluation study in 2002. The Navy is currently operating 24 P&T systems. Some of pump and treat system statistics from the review were:

- 79% were installed before 1999
- 79% were designed to operate for more than 5 years
- 66% were designed to operate for more than 10 years
- 58% were designed as ground water treatment systems
- 46% were designed as a interim action
- 82% conduct ground water monitoring annually
  - 46% conduct ground water monitoring semi annually
  - 36% conduct ground water monitoring quarterly
- 46% of the systems are operating at less than 75% design flow
- The construction costs for the 24 systems was \$61M
- The current O&M costs for the 24 systems is \$10M/year



**Table 10. Final Remedy Options for the NBVC MTBE Plume.**

Option	FY02 O&M Costs	LIFE CYCLE O&M COSTS/ SERVICE LIFE	ADVANTAGES	ISSUES
<p>Option 1:</p> <ul style="list-style-type: none"> <li>Continue to operate the pump and treat system.</li> <li>Remove the biobarrier in Dec 02 at the end of the ESTCP demonstration.</li> </ul>	\$250K	\$54 million/ 240 years	<ul style="list-style-type: none"> <li>Control and Containment system is located at leading edge of plume thereby preventing further migration of the plume.</li> <li>Acceptable to LARWQCB as interim remedy.</li> </ul>	<ul style="list-style-type: none"> <li>High O&amp;M costs/extended service life. Costs increase if GAC treatment is necessary.</li> <li>Disposes 1 million gallons of untreated water to sanitary sewer annually.</li> <li>Estimated time of 200 years for pump and treat system to capture 200 gallon MTBE mass between the system and the biobarrier, based on 3 years of monitoring data from biobarrier demonstrations. Cleanup cost <b>per gallon</b> of MTBE is \$270K.</li> <li>Removal of biobarrier will result in MTBE contaminated water flowing again from source zone.</li> <li>Removal of biobarrier creates a migration risk from future spills.</li> </ul>
<p>Option 2:</p> <ul style="list-style-type: none"> <li>Continue to operate the biobarrier.</li> <li>Turn off the MTBE Interim Plume Control and Containment System.</li> </ul>	\$75K	\$3 million/ 40 years	<ul style="list-style-type: none"> <li>Low O&amp;M costs; significantly shorter service life.</li> <li>Saves 10 million gallons of ground water annually.</li> <li>Cuts off source zone contamination; protects against future spills.</li> <li>Complete mineralization of MTBE to CO<sub>2</sub> and water.</li> </ul>	<ul style="list-style-type: none"> <li>Estimated mass of 200 gallons of MTBE will continue downgradient migration.</li> <li>Levine-Fricke (LFR) evaluated the plume migration, using the ground water flow model. It predicts MTBE may discharge into surface waters in concentrations in the 1300 to 1400 ppb range, exceeding LARWQCB proposed discharge standard of 5ppb. Eco-risk of MTBE to marine environment does not exceed acute (53 ppm) or chronic (18 ppm) aquatic criteria.</li> <li>Will require acceptance by LARWQCB.</li> </ul>
<p>Option 3:</p> <ul style="list-style-type: none"> <li>Continue to operate the biobarrier.</li> <li>Convert the pump and treat system to an air injection only biobarrier.</li> </ul>	\$125K for first 40 years; \$75K for remaining 200 years.	\$20 million/ 240 years	<ul style="list-style-type: none"> <li>Will contain both main source and leading edge of plume.</li> <li>Protects against future spills.</li> <li>No ground water or other disposal costs.</li> <li>Low capital and O&amp;M costs.</li> <li>Complete mineralization of MTBE at both locations to CO<sub>2</sub> and water.</li> </ul>	<ul style="list-style-type: none"> <li>Biobarrier studies conducted at Port Hueneme demonstrate that naturally occurring MTBE degraders are stimulated with addition of air or oxygen.</li> <li>Converting pump and treat system to air biobarrier will cost \$300K.</li> <li>Will require LARWQCB acceptance.</li> </ul>

## **6. IMPLEMENTATION ISSUES**

### **6.1 Cost Observations**

Project costs are sensitive to (a) depth to ground water and (b) site lithology. At this site, the deepest well drilled was to 20 ft bgs through unconsolidated sandy material, allowing the use of direct push methods. Surface installation also proved to be a substantially cost-saving measure.

### **6.2 Performance Observations**

This system was capable of degrading MTBE, BTEX, and TBA compounds to non-detect levels. Maximum regulated MTBE concentrations range from 5 to 560 ug-MTBE/L- ground water, and these are all greater than the concentrations leaving the down-gradient edge of the biobarrier.

It appears that biostimulation (aeration only) could be a viable option at many sites. In this demonstration, biostimulation was successful for treatment zones where the influent MTBE concentration was as great as 1,000 ug/L. It is not known if biostimulation would provide sufficient treatment for higher concentrations or fluxes. It is also not known how variable the performance of biostimulation might be from site to site. If bioaugmentation (addition of a microbial culture) is not required at a site, the installation costs will be lower, as discussed in Table 8, Section 5.2.

### **6.3 Scale-up**

This demonstration, at 500 ft, was a full-scale system. Most remediation systems at UST sites will likely be about 100 - 200 ft in length. The demonstration system was designed in a modular format (with 24- ft long replicated treatment systems) that is easily scaled to different sizes.

An important redundancy feature in this design is the gas injection system. Dissolved oxygen levels in the areas where pure oxygen is injected are in excess of 40 mg-oxygen/ L-ground water, and there is a reservoir of trapped gas pockets that can continue to feed oxygen to ground water. This can provide oxygen for several days if there is equipment failure, and there will not be any catastrophic change in dissolved ground water oxygen concentration (levels below 4 mg-oxygen/L-water).

To compensate for potential vertical variations in aquifer aeration (due to soil heterogeneity or well operation), the gas injection wells were spaced on 4-ft intervals in both the deep and shallow portions of the aquifer. This is a very conservative spacing, and likely the system would operate successfully with a larger spacing. The 4- ft spacing was selected for this site because the costs associated with well installation were minimal.

### **6.4 Other Significant Observations**

It is expected that this technology could be engineered to work in any setting, thus feasibility decisions are driven by economic considerations. With respect to economics, the two major

factors are the depth to ground water and soil lithology and these both affect the design and cost of gas injections wells.

## **6.5 Lessons Learned**

In this demonstration, biostimulation was successful for treatment zones where the influent MTBE concentration was as great as 1000 ug/L. It is not known if biostimulation would provide sufficient treatment for higher concentrations or fluxes. It is also not known how variable the performance of biostimulation might be from site to site.

At the demonstration site, concentrations >1,000 ug/L passed through the bioaugmented zone. The data clearly show significant treatment to non-detect levels with no apparent decline in activity during the lifetime of this test. Based on the results at Port Hueneme, it appears that biostimulation (aeration only) will be a viable option at some sites. However, one might have to wait longer for the desired treatment to be achieved; for example, in pilot test plots at Port Hueneme, it took 6-12 months for unseeded plots to achieve the same performance as seeded plots. A microcosm test can be conducted before system installation to assess the presence and activity of indigenous degraders. However if the site has immediate treatment time constraints imposed on it by a regulator, bioaugmentation may be the only option. It also is not clear if biostimulation would be sufficient for higher MTBE fluxes to the treatment system.

In this test, both oxygen and air were used in different areas to achieve oxygenation. Both sections of the barrier performed well, although both were not treating the same loading levels. Based on unpublished data from the pilot test plots, it appears that use of oxygen gas achieves a more uniform and high treatment effectiveness at Port Hueneme. At some sites (i.e., slow groundwater flow and sub-mg/L concentration levels), aeration with air may be sufficient. More study is needed on this topic. Use of an oxygen generator is more expensive in the short term, but it does provide some benefits not provided by air (i.e., if the system shuts down there is a larger oxygen reservoir to allow longer repair time, also the higher dissolved oxygen concentrations compensate for irregular gas distributions).

The presence of BTEX does not preclude the degradation of MTBE.

Although Schedule 40 PVC is easy to work with, it is not designed to carry air or oxygen under pressure unless it is buried. For the Port Hueneme biobarrier system, polyethylene tubing carries the air/O<sub>2</sub> from the buried PVC lines to the biobarrier tanks. Depending on the service life required, other materials such as stainless steel tubing could be utilized. It is also important not to restrict the diameter of the air lines from the satellite storage tanks to the injection wells, as the high-pressure short-duration flow to the wells is critical.

The oxygen generators are typically purchased as a turn key system. It is important to check the power coming into the site before ordering the oxygen generator system. On a military base, 208V power is common which can cause problems if the oxygen generator compressor is designed for 220V.

## 6.6 Approach to Regulatory Compliance and Acceptance

Permitting issues endemic to this technology involve those associated with well drilling/ waste disposal. Air and oxygen injection is not normally permitted. For bioaugmentation projects, microbe injection should be discussed with regulators during the design phase. For the Port Hueneme MTBE plume, the Los Angeles Regional Water Quality Control Board accepted the biobarrier technology as the final remedy for the MTBE plume.

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## **Appendix A**

### **ESTCP MTBE Biobarrier Demonstration Cost Summary**

ESTCP MTBE BIOBARRIER DEMONSTRATION COST SUMMARY SHEET				Material Costs Ver 2a.xls			
				Date:		2-Oct-02	
						Page 1 of 11	
Future System Note: Enter estimated length of future biobarrier system (in 50 foot increments) here:				500		feet	
This spreadsheet estimates above ground installation costs for aquifers less than 30 feet bgs.							